



US006436472B1

(12) **United States Patent**  
**Sago et al.**

(10) **Patent No.:** **US 6,436,472 B1**  
(45) **Date of Patent:** **Aug. 20, 2002**

(54) **METHOD OF APPLYING A COATING SOLUTION TO A SUBSTRATE SURFACE USING A ROTARY COATER**

5,260,174 A \* 11/1993 Nakazawa et al. .... 427/240  
5,374,312 A \* 12/1994 Hasebe et al. .... 118/52

(75) Inventors: **Hiroyoshi Sago; Shigemi Fujiyama; Futoshi Shimai; Akira Uehara**, all of Kanagawa (JP)

**FOREIGN PATENT DOCUMENTS**

DE 2746519 \* 4/1978 ..... 118/52  
JP 5-185020 \* 7/1993 ..... 427/240  
JP 6-103618 \* 4/1994 ..... 118/52

(73) Assignee: **Tokyo Ohka Kogyo Co., Ltd.**, Kanagawa (JP)

\* cited by examiner

(\* ) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 1184 days.

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(21) Appl. No.: **08/825,256**

(74) *Attorney, Agent, or Firm*—Carrier, Blackman & Associates, P.C.; Joseph P. Carrier; William D. Blackman

(22) Filed: **Mar. 27, 1997**

(57) **ABSTRACT**

**Related U.S. Application Data**

(63) Continuation of application No. 08/564,708, filed on Nov. 29, 1995, now abandoned.

A slit nozzle is positioned above an end of a glass substrate placed in an inner cup, and, while a coating solution is being ejected with reduced surface tension from the slit nozzle toward the glass substrate, the slit nozzle is translated parallel to the surface of the glass substrate to roughly coat the coating solution on substantially the entire surface of the glass substrate. Thereafter, the upper opening of the inner cup and the upper opening of an outer cup around the inner cup are closed by respective lids, and then the inner cup is rotated to rotate the glass substrate for thereby spreading the coated solution uniformly over the surface of the glass substrate under centrifugal forces.

(30) **Foreign Application Priority Data**

Nov. 29, 1994 (JP) ..... 6-295143  
Feb. 27, 1995 (JP) ..... 7-038350

(51) **Int. Cl.**<sup>7</sup> ..... **B05D 3/12**

(52) **U.S. Cl.** ..... **427/240; 118/52**

(58) **Field of Search** ..... 118/52; 427/240

(56) **References Cited**

**U.S. PATENT DOCUMENTS**

5,234,499 A \* 8/1993 Sasaki et al. .... 427/240

**17 Claims, 6 Drawing Sheets**

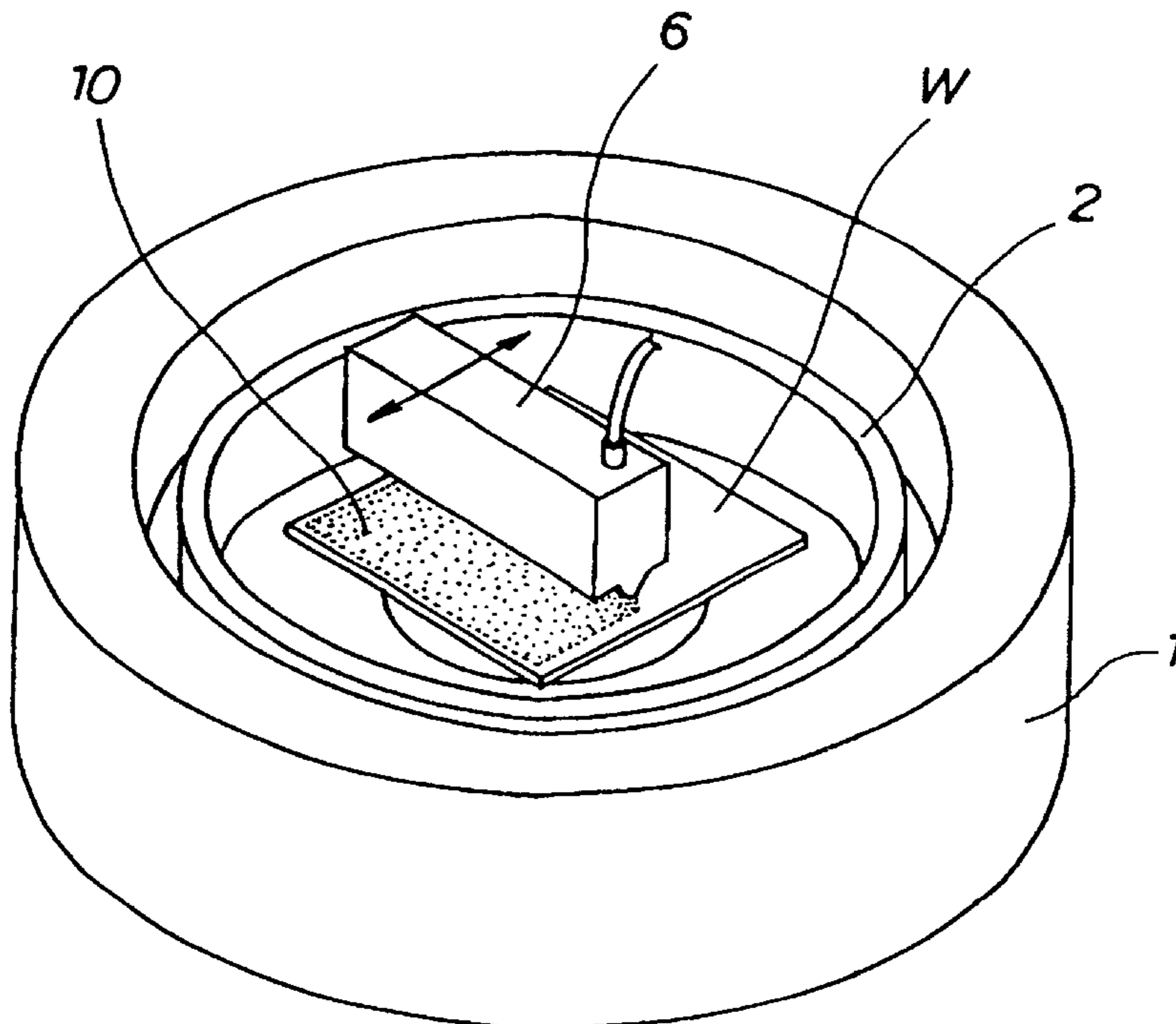


FIG. 1

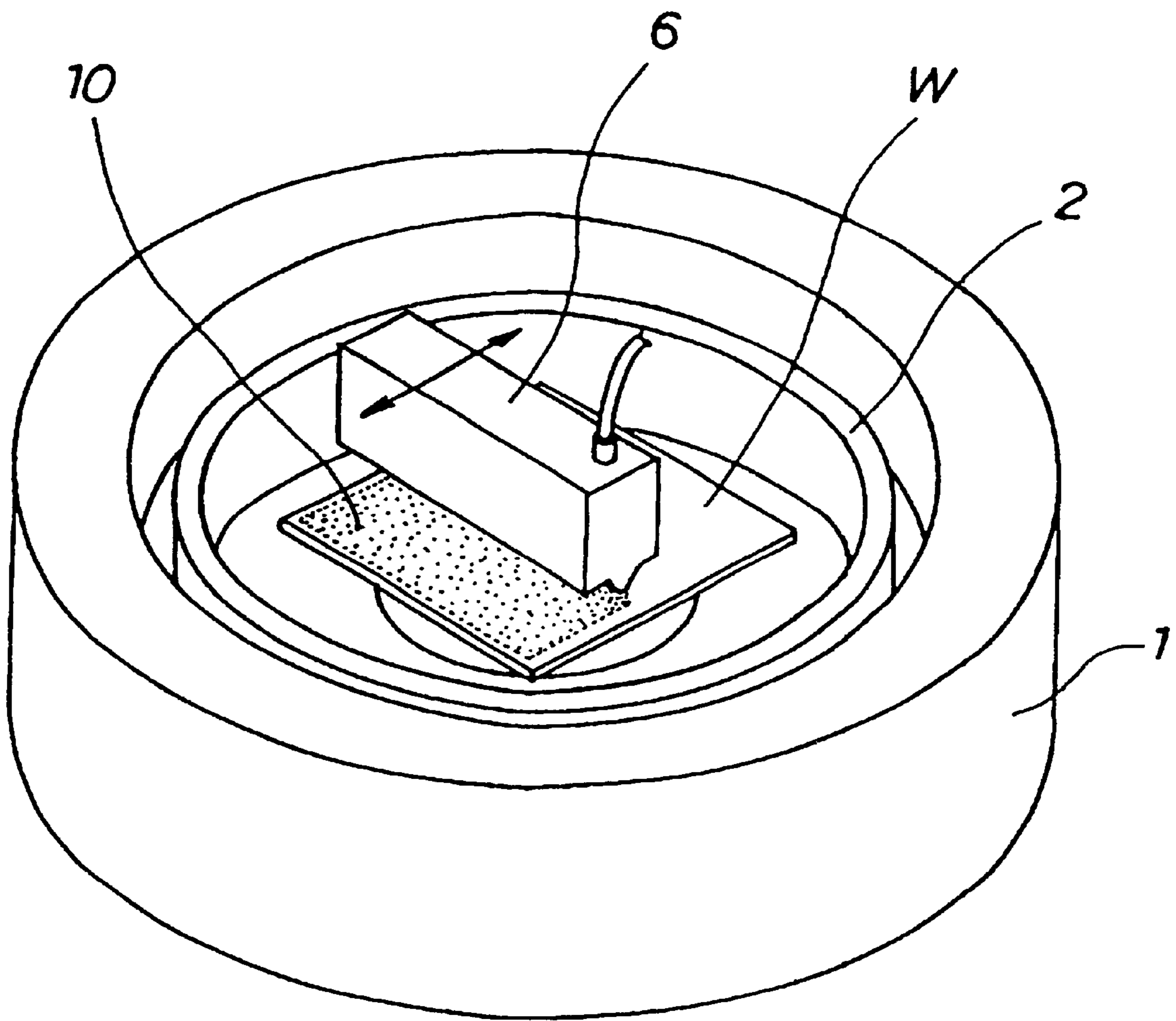


FIG. 2

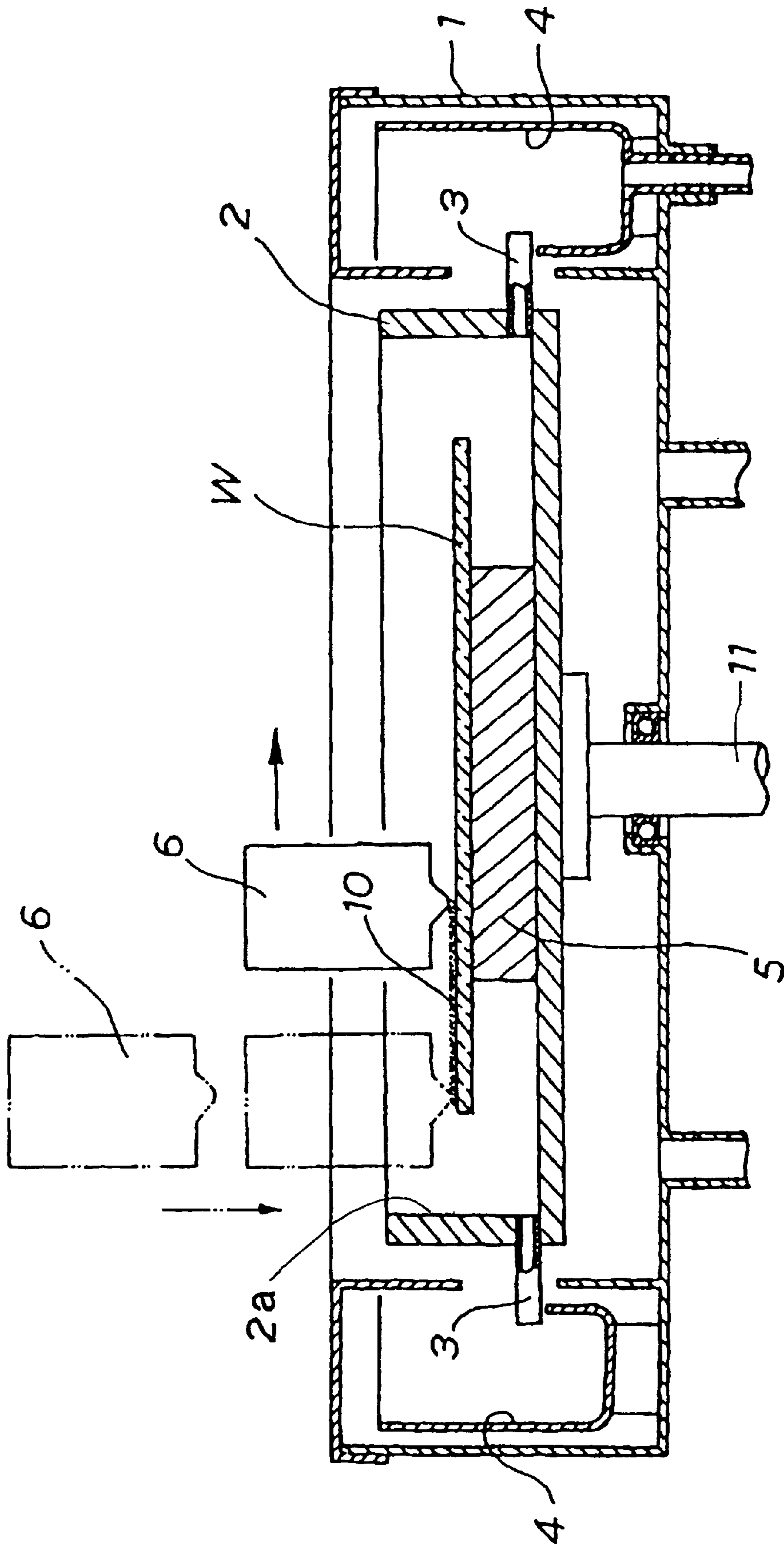


FIG. 3

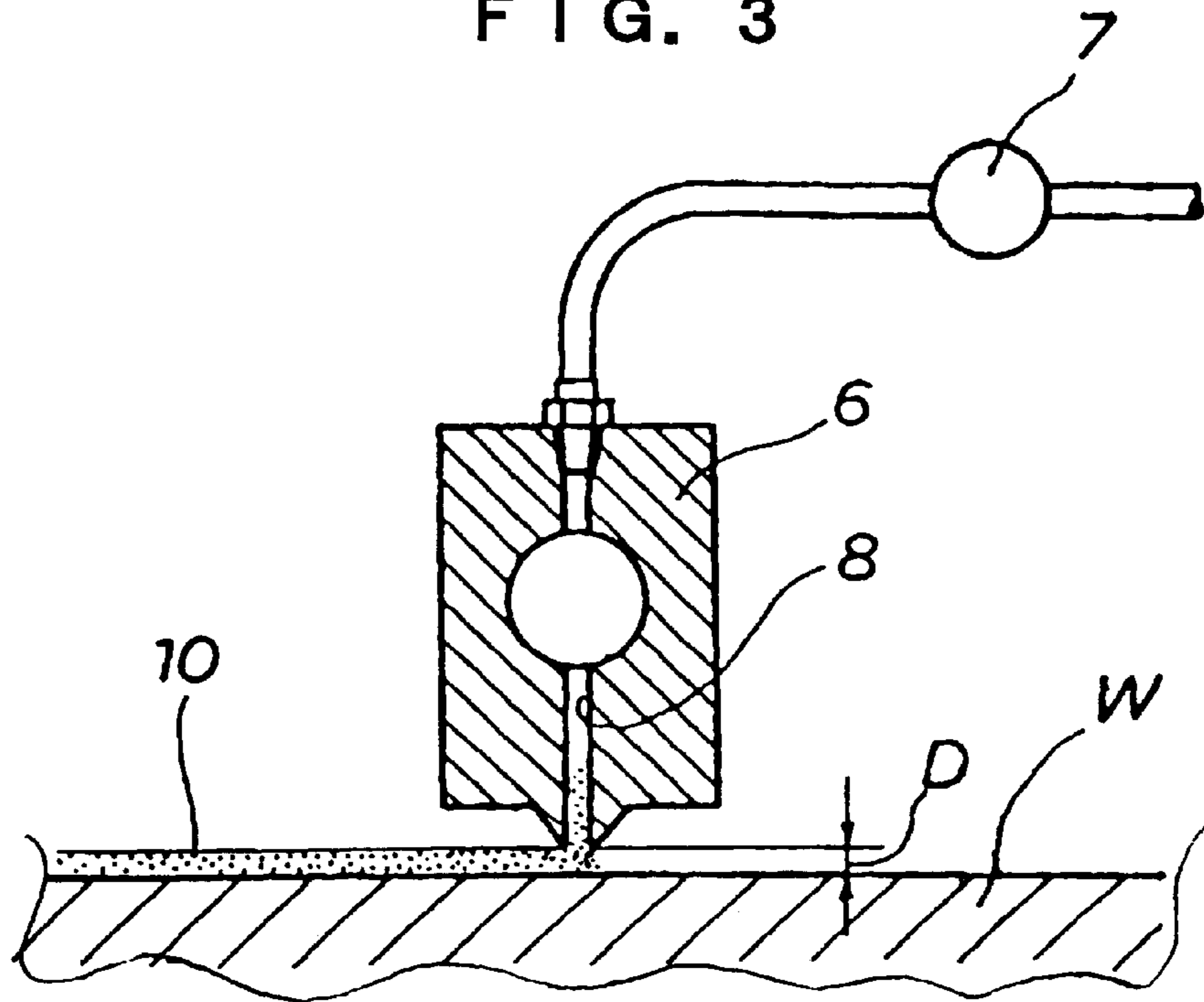


FIG. 4

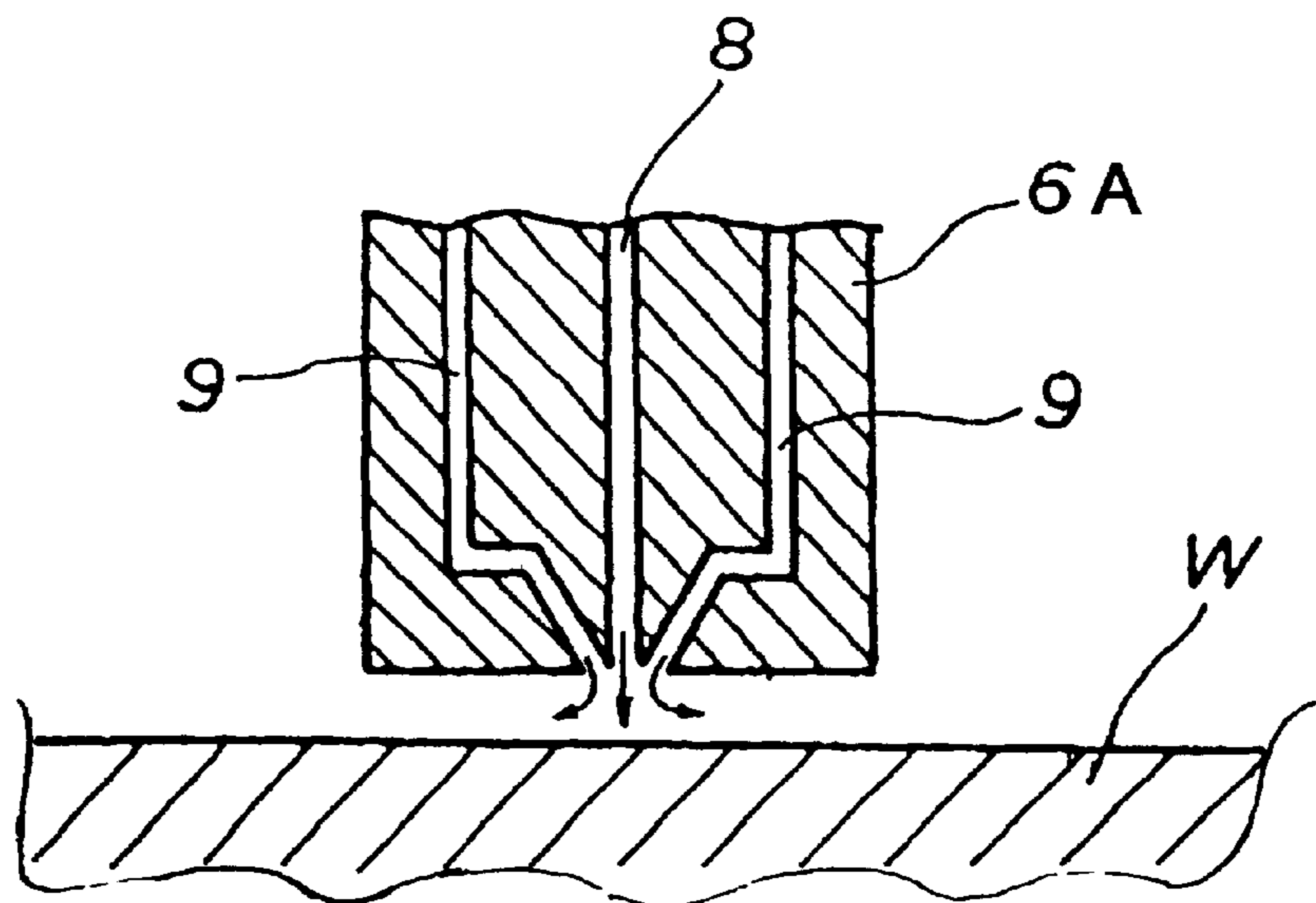


FIG. 5

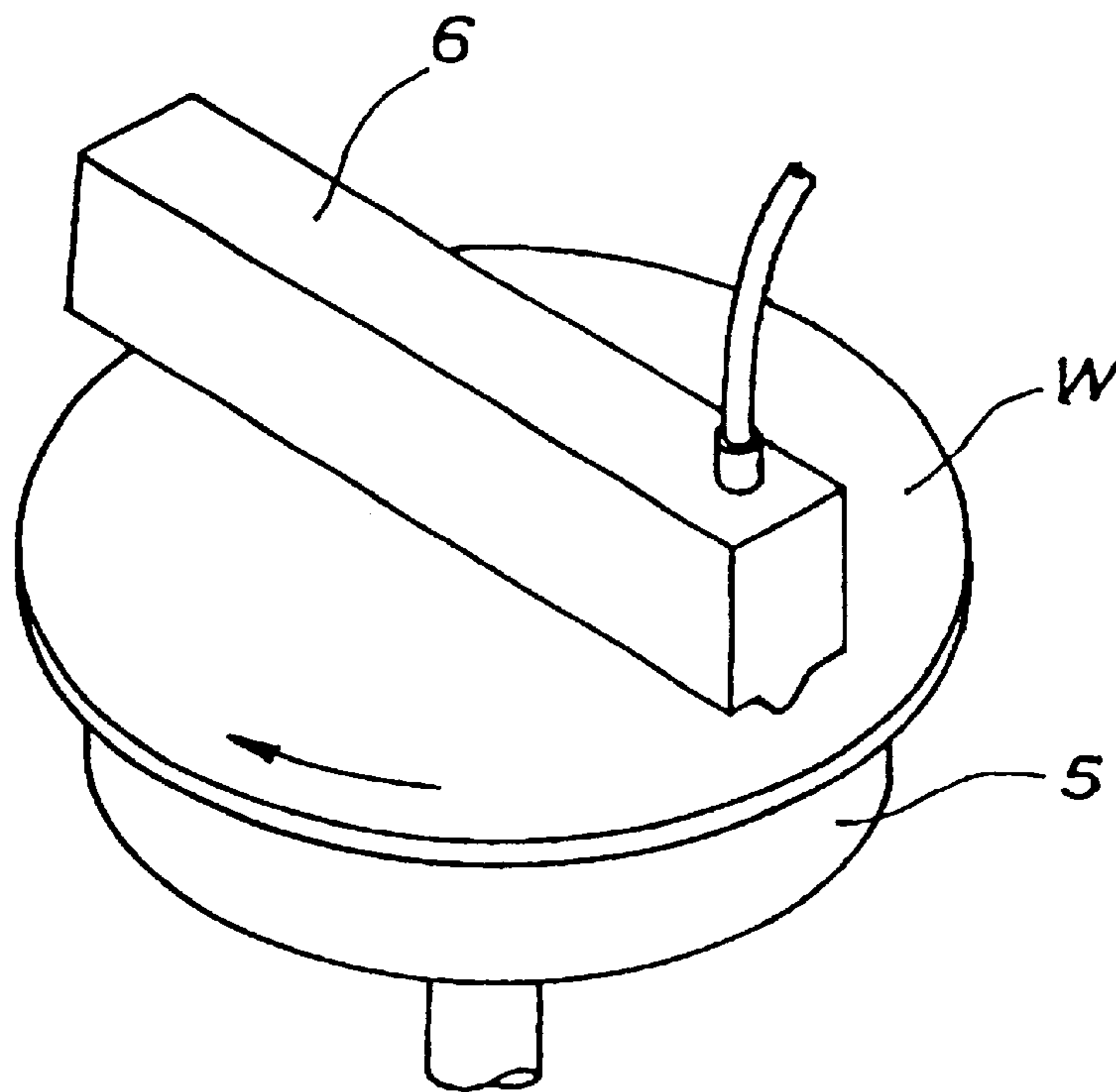


FIG. 8

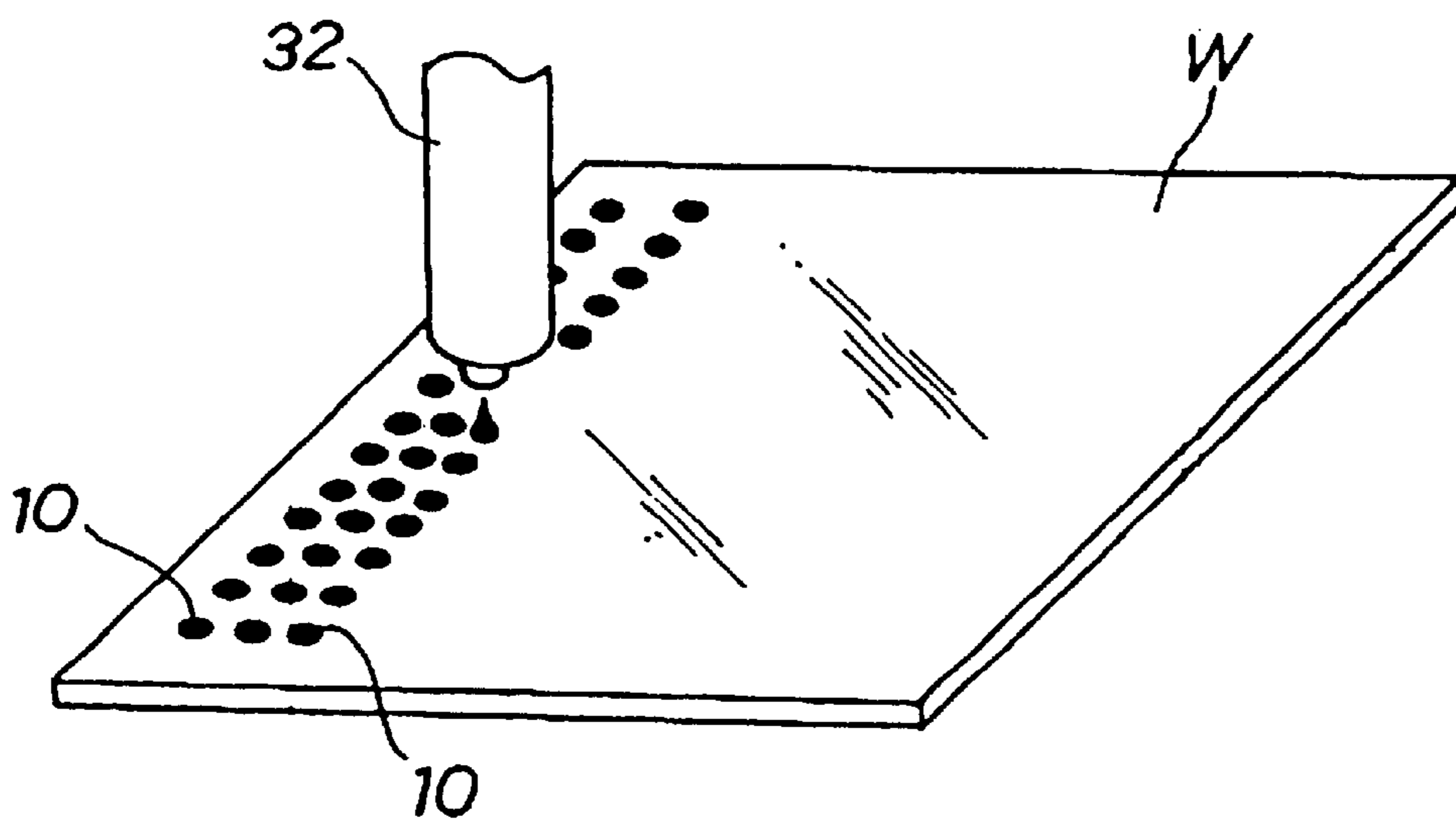
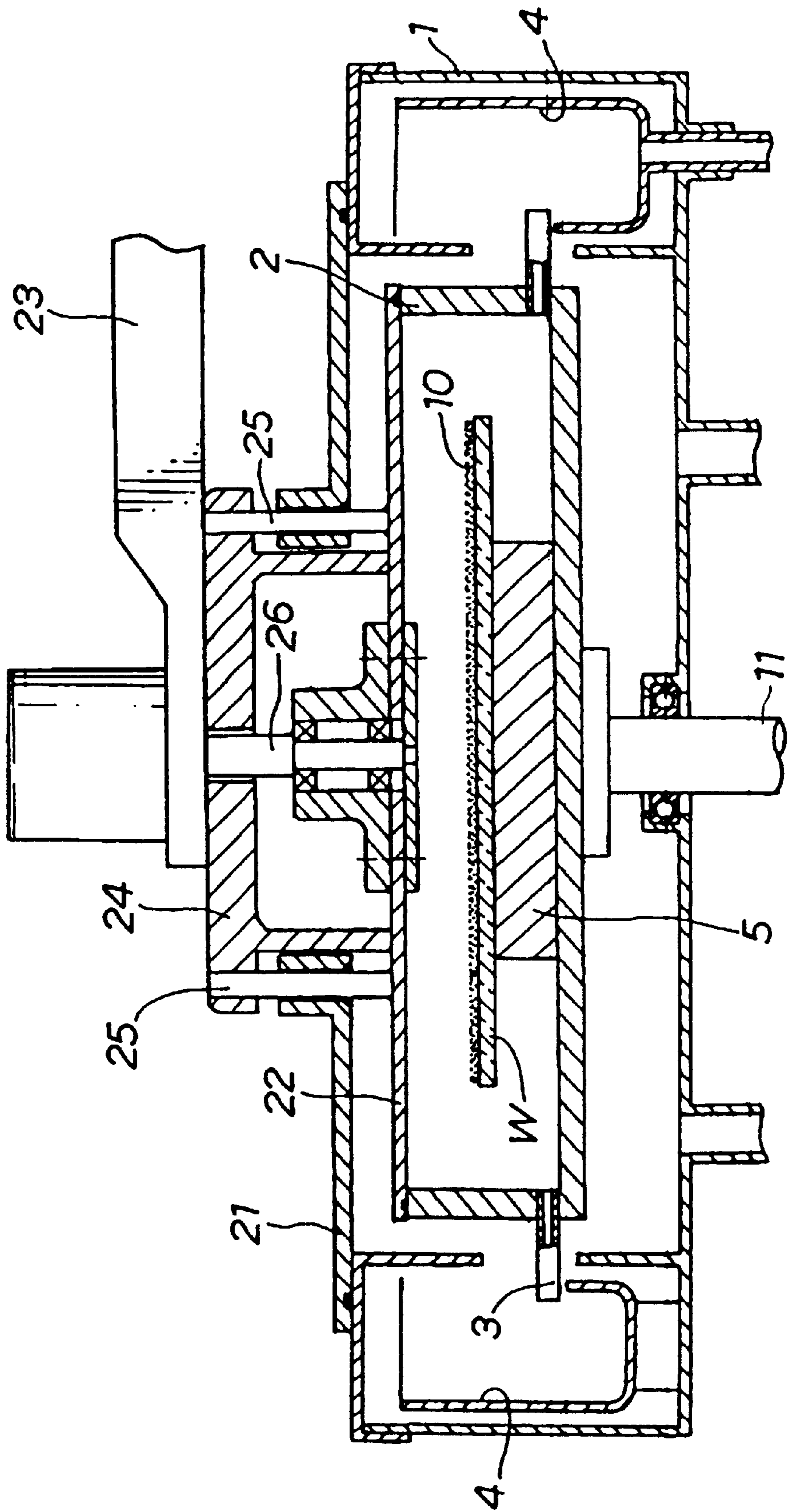




FIG. 6







**METHOD OF APPLYING A COATING  
SOLUTION TO A SUBSTRATE SURFACE  
USING A ROTARY COATER**

This application is a continuation of U.S. application Ser. No. 08/564,708, filed Nov. 29, 1995, now abandon.

**BACKGROUND OF THE INVENTION**

**1. Field of the Invention**

The present invention relates to a method of coating a coating solution such as a photoresist to the surface of a substrate such as a glass substrate, a semiconductor wafer, or the like.

**2. Description of the Related Art**

Photoresists for forming color filters are uniformly coated on the surface of a glass substrate for use in liquid-crystal display devices, and various coating solutions are uniformly coated on the surface of a semiconductor wafer. It has been customary to apply a uniform coating of such a coating solution by dropping the coating solution onto the center of the substrate and then rotating, with a spinner, the substrate to spread the dropped coating solution uniformly over the entire surface of the substrate under centrifugal forces.

According to the above coating process using a spinner, a large amount of coating solution tends to be scattered off the substrate because it is necessary to spread the coating solution dropped onto the center of the substrate uniformly outwardly to the peripheral edge of the substrate. As a result, the coating solution is consumed in a large quantity.

Use of a slit nozzle for minimizing the amount of coating solution consumed is disclosed in Japanese laid-open patent publications Nos. 63-156320, 4-332116, and 6-151296.

According to the processes disclosed in Japanese laid-open patent publications Nos. 63-156320 and 4-332116, while the slit nozzle positioned above a substrate is being translated parallel to the substrate, a coating solution is dropped from the slit nozzle onto the substrate. After the coating solution is deposited to a somewhat uniform thickness on the surface of the substrate, the substrate is rotated to uniformize the thickness of the coating solution thereon. However, since the coating solution is simply dropped on the surface of the substrate, the coating solution cannot completely uniformly be deposited because of the surface tension of the dropped coating solution. Therefore, it is necessary to apply a large amount of coating solution in order to form a uniform film of coating solution on the substrate. Another problem is that because the substrate is rotated in an atmosphere vented to the ambient air, the solvent in the coating solution tends to be evaporated quickly, making the coating solution more viscous soon. Therefore, it soon becomes difficult to spread the coating solution uniformly over the entire surface of the substrate.

According to the process revealed in Japanese laid-open patent publication No. 6-151296, the tip end of the slit nozzle is used to uniformize the thickness of a film of coating solution on the surface of a substrate. However, the slit nozzle is liable to be smeared with coating solution as its tip end contacts the coating solution. Further, the coated film tends to become irregular in thickness when the slit nozzle is lifted off the coating solution after the coating solution is deposited on the substrate.

**SUMMARY OF THE INVENTION**

It is therefore an object of the present invention to provide a method of coating a coating solution quickly to a thin uniform thickness on the surface of a substrate.

According to an aspect of the present invention, there is provided a method of coating a solution on a surface of a rectangular substrate, comprising the steps of positioning a slit nozzle above the rectangular substrate, ejecting the solution from the slit nozzle toward the surface of the rectangular substrate while reducing or minimizing the surface tension of the solution, translating the slit nozzle parallel to the rectangular substrate to coat the solution on substantially the entire surface of the rectangular substrate while the solution is being ejected from the slit nozzle, and thereafter rotating the rectangular substrate to spread the solution uniformly over the surface of rectangular substrate.

According to another aspect of the present invention, there is also provided a method of coating a solution on a surface of a circular substrate, comprising the steps of positioning a slit nozzle above the circular substrate, ejecting the solution from the slit nozzle toward the surface of the circular substrate while reducing or minimizing the surface tension of the solution, rotating the circular substrate at a first speed to coat the solution on substantially the entire surface of the circular substrate while the solution is being ejected from the slit nozzle, and thereafter rotating the circular substrate at a second speed greater than said first speed to spread the solution uniformly over the surface of circular substrate.

The surface tension of the solution may be reduced or minimized by reducing the distance between a lower end of the slit nozzle and the surface of the substrate and pressurizing the solution. Specifically, when the solution has a viscosity of at most 10 cP, it may be pressurized under a pressure ranging from 0.5 kg/cm<sup>2</sup> to 10 kg/cm<sup>2</sup>, and the distance between the lower end of the slit nozzle and the surface of the substrate may be at most 10 mm.

According to still another aspect of the present invention, there is also provided a method of coating a solution on a surface of a rectangular or circular substrate, comprising the steps of setting the rectangular or circular substrate in a rotary cup, roughly coating the solution on substantially the entire surface of the rectangular or circular substrate, and thereafter rotating said rotary cup to spread the coated solution uniformly over the surface of the rectangular or circular substrate under centrifugal forces. It is preferable to close an upper opening of the rotary cup before the rotary cup is rotated.

According to yet still another aspect of the present invention, there is also provided a method of coating a solution on a surface of a rectangular or circular substrate, comprising the steps of roughly coating the solution on substantially the entire surface of the rectangular or circular substrate, immediately thereafter setting the rectangular or circular substrate in a rotary cup, and then rotating said rotary cup to spread the coated solution uniformly over the surface of the rectangular or circular substrate under centrifugal forces. It is preferable to close an upper opening of the rotary cup before the rotary cup is rotated.

The solution may be roughly coated on substantially the entire surface of the rectangular or circular substrate by a slit nozzle, a jet nozzle, a roll coater, or a bar coater.

Since the distance between the lower end of the slit nozzle and the surface of the substrate is reduced and the solution is pressurized, according to some of the aforementioned aspects of the invention, it is possible to apply, to the solution, forces tending to cancel out or minimize effects of the surface tension of the solution when it is brought into contact with the surface of the substrate.

After the rectangular or circular substrate is set in the rotary cup, the upper opening of the rotary cup is preferably



closed and then the rotary cup is rotated to spread the solution uniformly over the rectangular or circular substrate under centrifugal forces according to other aforementioned aspects of the invention. Therefore, it is possible to spread the solution over the substrate in an atmosphere which makes it difficult to dry the solution.

The above and further objects, details and advantages of the present invention will become apparent from the following detailed description of preferred embodiments thereof, when read in conjunction with the accompanying drawings.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a perspective view of a rotary-cup coating apparatus used to carry out a coating method according to an embodiment of the present invention;

FIG. 2 is a vertical cross-sectional of the coating apparatus shown in FIG. 1;

FIG. 3 is a cross-sectional view of a slit nozzle used in the coating apparatus shown in FIG. 1;

FIG. 4 is an enlarged fragmentary cross-sectional view of a slit nozzle according to another embodiment of the present invention;

FIG. 5 is a perspective view showing the manner in which a coating solution is coated on a semiconductor wafer by the coating apparatus;

FIG. 6 is a vertical cross-sectional view of a rotary-cup coating apparatus with a lid assembly according to still another embodiment of the present invention;

FIG. 7 is a vertical cross-sectional view showing the manner in which a coating solution is roughly coated on a substrate outside of the rotary-cup coating apparatus shown in FIG. 6; and

FIG. 8 is a perspective view showing the manner in which a coating solution is roughly coated substantially entirely on the surface of a glass substrate by a jet nozzle.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

FIGS. 1 through 3 show a rotary-cup coating apparatus used to carry out a coating method according to an embodiment of the present invention.

As shown in FIGS. 2 and 3, the rotary-cup coating apparatus has an outer cup 1 and an inner cup 2 disposed in the outer cup 1 and rotatable by a spinner 11.

Drain pipes 3 extend radially outwardly from a circumferential wall 2a of the inner cup 2 and have outer distal ends opening in an annular liquid retrieval passage 4 disposed in the outer cup 1. A chuck 5 for attracting and holding a rectangular glass substrate W thereon is disposed centrally in the inner cup 2.

A slit nozzle 6 is normally disposed upwardly of the inner cup 2. The slit nozzle 6 is supported on an arm (not shown) which can be moved to displace the slit nozzle 6 in vertical directions and also horizontal directions parallel to the upper surface of the glass substrate W.

The slit nozzle 6 is supplied with a coating solution through a pressurizing unit 7 (see FIG. 3). As shown in FIG. 3, the slit nozzle 6 has a single nozzle hole 8 defined vertically therein for ejecting the coating solution supplied through the pressurizing unit 7. The nozzle hole 8 has a slit of certain width which is open at the lower end of the slit nozzle 6.

FIG. 4 shows a slit nozzle 6A according to another embodiment of the present invention. The slit nozzle 6A

may, as depicted have a central nozzle hole 8 defined therein and a pair of gas ejection holes 9 defined therein one on each side of, i.e., forward and backward of, the central nozzle hole 8. When the gas ejection holes 9 eject a gas from their lower ends, the ejected gas tends to draw a coating solution from the central nozzle hole 8.

In the slit nozzles 6, 6A shown in FIGS. 3 and 4, a plurality of nozzle holes may be defined instead of the single nozzle hole 8.

According to the coating method of the invention, a coating solution is coated on the glass substrate W by the coating apparatus as follows:

As shown in FIG. 2, the slit nozzle 6 is positioned closely above an end of the glass substrate W. While a coating solution 10 which is pressurized by the pressurizing unit 7 is being ejected from the slit nozzle 6 toward the glass substrate W, the slit nozzle 6 is translated parallel to the glass substrate W. The slit nozzle 6 is moved to the other end of the glass substrate W while ejecting the coating solution 10 under pressure until the coating solution 10 is applied to substantially the entire upper area of the glass substrate W. Thereafter, the inner cup 2 is rotated about its center by the spinner 11 to rotate the glass substrate W therewith for thereby spreading the applied coating solution 10 uniformly over the upper surface of the glass substrate W under centrifugal forces.

Since the inner cup 2 and the glass substrate W are rotated in unison with each other, any turbulent air flows over the glass substrate W are minimized, allowing the coating solution 10 to be formed into a uniform coated film on the glass substrate W.

In the above coating method, the slit nozzle 6 starts and stops applying the coating solution 10 in positions directly above the opposite ends of the glass substrate W. However, the slit nozzle 6 may start and stop applying the coating solution 10 in positions that are spaced outwardly from the opposite ends of the glass substrate W. With such a modified coating process, it is possible to coat the coating solution uniformly up to the ends of the glass substrate W though a certain amount of coating solution is wasted because it is ejected from the slit nozzle 6 even when the slit nozzle 6 is positioned off the opposite ends of the glass substrate W.

Before the applied coating solution is uniformly spread over the glass substrate W upon rotation thereof, it is preferable to apply the coating solution in as thin and uniform a films as possible on the glass substrate W with the slit nozzle 6. To this end, the surface tension of the coating solution should be reduced when the coating solution is ejected from the slit nozzle 6 toward the surface of the glass substrate W.

Factors involved in the surface tension of the coating solution include (1) the viscosity (cP) of the coating solution, (2) the pressure (kg/cm<sup>2</sup>) applied to the coating solution, (3) the distance (mm) between the lower end of the slit nozzle and the surface of the substrate, (4) the speed at which the slit nozzle moves, (5) the surface roughness of the substrate, and (6) the temperature.

A photoresist for forming a color filter, for example, has a normal viscosity of 10 cP or less. If the above factors or conditions (4) through (6) are fixed with respect to a coating solution whose viscosity is 10 cP or less, then the pressure P applied to the coating solution should preferably range from 0.5 (kg/cm<sup>2</sup>) to 10 (kg/cm<sup>2</sup>), and the distance D between the lower end of the slit nozzle and the surface of the substrate should preferably be of 10 (mm) or less. Generally, the distance D should be as small as possible.



However, if the distance  $D$  were too small, the coating solution would be deposited on and tend to smear a lower surface of the slit nozzle. Therefore, the distance  $D$  should be of a value which falls in a range not to deposit the coating solution to the lower surface of the slit nozzle.

Since the distance between the lower end of the slit nozzle **6** and the glass substrate  $W$  is relatively small and the coating solution ejected from the slit nozzle **6** is pressurized by the pressurizing unit **7**, forces act on the ejected coating solution to cancel out or minimize the surface tension of the coating solution. Consequently, the coating solution can be coated quickly as a thin and uniform film on the surface of the glass substrate  $W$ , and the amount of the coating solution that is consumed to coat the glass substrate  $W$  is greatly reduced.

FIG. **5** shows the manner in which a coating solution is coated on a rotating circular semiconductor wafer  $W$  as the substrate. In FIG. **5**, the slit nozzle **6** is positioned above the semiconductor wafer  $W$ . While a coating solution of reduced surface tension is being ejected from the slit nozzle **6**, the semiconductor wafer  $W$  on the chuck **5** is rotated at a low speed. After the coating solution has been applied to substantially the entire surface of the semiconductor wafer  $W$ , the semiconductor wafer  $W$  is rotated at a high speed, greater than the low speed, to spread the coating solution uniformly over the surface of the semiconductor wafer  $W$ .

An experiment was conducted to evaluate the uniformities of coated films on glass substrates when a coating solution was dropped under different pressures and in different quantities. Specifically, a photoresist having a viscosity of 6.5 cP for forming a color filter was coated on a glass substrate having a size of 200 mm×200 mm by the slit nozzle shown in FIG. **4** at a temperature of 23° C. and a humidity of 50%, when the slit nozzle was moved at a speed of 500 mm/s and spaced from the glass substrate by a distance of 5 mm. After the photoresist was coated at different pressures (kg/cm<sup>2</sup>) applied thereto and in different dropped quantities (g), glass substrates were rotated at 700 rpm for 6 seconds. The uniformities of coated films on the glass substrates are given in the following table:

Pressure (kg/cm <sup>2</sup> )	0.6	0.7	0.8	0.9	1.0
Dropped quantity (g)	0.72	0.85	1.02	1.15	1.26
Average film thickness (μm) before being rotated	2.80	3.35	4.10	4.68	5.18
Uniformity (±%)	13.8	14.1	7.93	11.2	5.31
Average film thickness (μm) after being rotated	1.80	1.82	1.81	1.84	1.80
Uniformity (±%)	10.3	5.78	2.76	2.72	3.05

When a conventional slit nozzle was used, a pressure of 1.0 kg/cm<sup>2</sup> was required to be applied to the coating solution, and 3.00 g of a photoresist was needed to cover the entire surface of the glass substrate. With the conventional slit nozzle, the average film thickness was 1.82 μm, and the uniformity was ±2.84%.

FIG. **6** shows of a rotary-cup coating apparatus according to still another embodiment of the present invention. The rotary-cup coating apparatus shown in FIG. **6** has a lid assembly composed of lids **21**, **22** for closing the respective upper openings of outer and inner cups **1**, **2**. The rotary-cup coating apparatus also includes an arm **23** which is movable linearly, angularly, and/or vertically, and a support block **24** fixed to a distal end of the arm **23**. The lid **21** for closing the upper opening of the outer cup **1** is vertically slidably attached to the support block **24** by pins **25**, and the lid **22**

for closing the upper opening of the inner cup **2** is rotatably mounted on a shaft **26** disposed centrally on the support block **24**.

To close the upper openings of the outer and inner cups **1**, **2**, the arm **23** is moved to position the lids **21**, **22** above the outer and inner cups **1**, **2**, and then is lowered. When the arm **23** is lowered, the lid **21** closes the upper opening of the outer cup **1**. Upon continued descent of the arm **23**, the support block **24** and the lid **22** are lowered until the lid **22** closes the upper opening of the inner cup **2**.

After the upper openings of outer and inner cups **1**, **2** have been closed respectively by the lids **21**, **22**, the concentration of volatilized solvent from the coating solution in the inner cup **2** is increased, and any evaporation of the solvent from the coating solution is minimized. Therefore, the coating solution does not become excessively viscous and can smoothly be spread over the glass substrate  $W$ .

A flow-rectifying plate (not shown) may be attached to the lower surface of the lid **22**. When the lid **22** is closed, only a small gap is created between the flow-rectifying plate and the glass substrate  $W$  while the flow rectifying plate and the substrate  $W$  are rotated together, for thereby preventing turbulent air flows from being developed in the inner cup **2**. Therefore, a more uniformly coated film can be produced on the glass substrate  $W$ .

FIG. **7** shows a coating method according to another embodiment of the present invention. In the previous embodiments, a coating solution is applied to substantially the entire surface of a substrate within the rotary-cup coating apparatus. According to the embodiment shown in FIG. **7**, however, a coating station **30** is located outside of the rotary-cup coating apparatus shown in FIG. **6**. In the coating station **30**, a coating solution **10** is roughly or non-uniformly coated on substantially the entire surface of a substrate  $W$  by a roll coater **31**, for example. Thereafter, the substrate  $W$  is taken out of the coating station **30**, and set in the inner cup **2** of the rotary-cup coating apparatus. Then, the upper openings of outer and inner cups **1**, **2** are closed respectively by the lids **21**, **22**, and the inner cup **2** is rotated to spread the roughly applied coating solution **10** uniformly over the surface of the substrate  $W$  under centrifugal forces.

In the above embodiments, the slit nozzles **6**, **6A** and the roll coater **31** are illustrated as means for roughly coating the coating solution on substantially the entire surface of the substrate  $W$ . However, as shown in FIG. **8**, a jet nozzle **32** may be used to apply dots of coating solution **10** to substantially the entire surface of the substrate  $W$ , and after the dots of coating solution **10** have been applied, the substrate  $W$  may be rotated to spread the coating solution **10** uniformly over the surface of the substrate  $W$  under centrifugal forces.

Alternatively, a bar coater, a flow coater, a sprayer an electrostatic coating device, or the like may be used as means for roughly coating the coating solution on substantially the entire the surface of the substrate  $W$ .

Although there have been described what are at present considered to be the preferred embodiments of the invention, it will be understood that the invention may be embodied in other specific forms without departing from the essential characteristics thereof. The present embodiments are therefore to be considered in all respects as illustrative, and not restrictive. The scope of the invention is indicated by the appended claims rather than by the foregoing description.

What is claimed is:

1. A method of coating a solution on a surface of a non-circular substrate, comprising the steps of:



positioning a slit nozzle above the substrate;

ejecting the solution from the slit nozzle toward the surface of the substrate so as to minimize effects of surface tension of the solution when the solution is brought into contact with the surface of the substrate;

translating the slit nozzle parallel to the substrate to coat the solution on substantially the entire surface of the substrate while the solution is being ejected from the slit nozzle without interruption, and while maintaining a tip end of said nozzle out of contact with said solution after the solution is ejected from the nozzle; and

thereafter rotating the substrate to spread the solution uniformly over the surface of the substrate.

2. A method according to claim 1, wherein the surface tension of the solution is minimized by setting a distance between a lower end of the slit nozzle and the surface of the substrate to a value  $\leq 10$  mm and by pressurizing the solution.

3. A method according to claim 2, wherein said solution has a viscosity of at most 10 cP and is pressurized under a pressure ranging from 0.5 kg/cm<sup>2</sup> to 10 kg/cm<sup>2</sup>, and the distance between the lower end of the slit nozzle and the surface of the substrate is at most 10 mm.

4. A method according to claim 2, wherein said distance is sufficiently large to prevent said slit nozzle from being smeared with solution coated on the substrate.

5. A method according to claim 1, wherein said substrate is rectangular.

6. A method of coating a solution on a surface of a circular substrate, comprising the steps of:

positioning a slit nozzle above the circular substrate;

ejecting the solution from the slit nozzle toward the surface of the circular substrate so as to minimize effects of surface tension of the solution when the solution is brought into contact with the surface of the substrate;

rotating the circular substrate at a first speed to coat the solution on substantially the entire surface of the circular substrate while the solution is being ejected from the slit nozzle without interruption, and while maintaining a tip end of said nozzle out of contact with said solution after the solution is ejected from the nozzle; and

thereafter rotating the circular substrate at a second speed greater than said first speed to spread the solution uniformly over the surface of the circular substrate.

7. A method according to claim 6, wherein the surface tension of the solution is minimized by setting a distance between a lower end of the slit nozzle and the surface of the substrate to a value  $\leq 10$  mm and by pressurizing the solution.

8. A method according to claim 7, wherein said solution has a viscosity of at most 10 cP and is pressurized under a pressure ranging from 0.5 kg/cm<sup>2</sup> to 10 kg/cm<sup>2</sup>, and the distance between the lower end of the slit nozzle and the surface of the substrate is at most 10 mm.

9. A method of coating a solution on a surface of a substrate, comprising the steps of;

non-uniformly coating the solution on substantially the entire surface of the substrate using a slit nozzle by ejecting without interruption the solution from the slit nozzle toward the surface of the substrate so as to cancel out surface tension of the solution when the solution is brought into contact with the surface of the substrate, and while maintaining a tip end of said nozzle out of contact with the solution after the solution is ejected from the nozzle; and

thereafter rotating said substrate to spread the non-uniformly coated solution over the surface of the substrate under centrifugal forces.

10. A method according to claim 9, further comprising the step of:

closing an upper opening of said rotary cup with a lid before the rotary cup is rotated.

11. A method according to claim 9, further including the step of:

setting the substrate in said rotary cup before said step of non-uniformly coating the substrate.

12. A method according to claim 9, further including the step of:

setting the substrate in said rotary cup immediately after said step of non-uniformly coating the substrate.

13. A method according to claim 9, wherein said substrate is fully enclosed within said rotary cup during said rotating step.

14. A method according to claim 13, including a step of providing means which operatively cooperate with said rotating cup for preventing turbulent airflows from being developed within said rotary cup during said rotating step.

15. A method according to claim 9, wherein said substrate is rectangular or circular in shape.

16. A method according to claim 9, wherein said step of non-uniformly coating a substrate involves rotating said substrate at a first speed while the solution is non-uniformly coated on substantially the entire surface of the substrate, and thereafter the substrate is rotated at a second speed greater than the first speed during said rotating step.

17. A method according to claim 9, wherein the solution is ejected from the nozzle so as to cancel out effects of the surface tension of the solution when the solution is brought into contact with the surface of the substrate.



UNITED STATES PATENT AND TRADEMARK OFFICE  
**CERTIFICATE OF CORRECTION**

PATENT NO. : 6,436,472 B1  
DATED : August 20, 2002  
INVENTOR(S) : Hiroyoshi Sago et al.

Page 1 of 1

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 2,

Line 12, change "of rectangular" to -- of the rectangular --.  
Line numbered between 24 and 25, before "circular" insert -- the --.  
Line 61, after "pressurized" delete the comma.

Column 3,

Line 17, after "cross-sectional" insert -- view --.

Column 4,

Line 1, after "depicted" insert a comma.  
Line 47, change "films" to -- film --.  
Line 65, change "be" to -- of --.  
Line 66, change "of" to -- be --.

Column 5,

Line 58, delete "of".

Column 6,

Line numbered between 20 and 21, between "W" and "while" insert a comma.  
Line 52, after "sprayer" insert a comma.  
Line 55, change "the surface" to -- surface --.

Column 8,

Line 7, change "of;" to -- of: --.  
Line 18, after "solution" insert -- uniformly -- .

Signed and Sealed this

Twenty-fifth Day of March, 2003



JAMES E. ROGAN  
*Director of the United States Patent and Trademark Office*